

Solid-State Inorganic Nanofiber-Polymer Composite Electrolytes for Lithium Ion Batteries

PI: Nianqiang Wu
West Virginia University

2019 DOE Vehicle Technologies Office Annual Merit Review
June 10th, 2019

Project ID: **bat321**

Overview

Timeline

- Project Start Date: Oct. 1, 2016
- Project End Date: Sept. 30, 2019
- Percent complete: 83% till 04/12/2019. We will complete 100% by Sept 30, 2019

Budget

- Total project funding
 - DOE share:\$1,244,012
 - Contractor share: \$156,181
- Funding received in FY 2018: : \$463,711
- Funding for FY 2019: \$456,762

Barriers

- Poor conductivity of current composite electrolytes (10^{-6} S/cm to 10^{-4} S/cm)
- Low mechanical strength of composite electrolytes
- Low stability during operation

Interactions/collaborations:

North Carolina State University

Project lead:

West Virginia University

Relevance

Overall objectives

Develop the solid-state electrolytes by integrating a highly-conductive inorganic nanofibrous network in a conductive polymer matrix for both lithium metal and lithium-sulfur batteries.

Objectives of this period (04/01/2018– 03/31/2019)

- Construct and test the Li metal/composite electrolyte/Li metal symmetric cells;
- Construct and test the Li metal/composite electrolyte/cathode full cells;
- Optimize the ceramic-polymer composite electrolytes.

Impact

The DOE funding will allow the research team to develop solid-state inorganic nanofiber-polymer composite electrolytes that will not only provide higher ionic conductivity, improved mechanical strength and better stability than the PEO-based polymer electrolyte, but also exhibit better mechanical integrity, easier incorporation and better compatibility with the lithium metal anode than the planar ceramic membrane counterparts. The proposed inorganic nanofiber-polymer composite electrolytes will enable the practical use of high energy-density, high power-density lithium metal batteries and lithium-sulfur batteries.

Milestones

Milestones in Year 1-(10/01/2016– 9/31/2017)

For polymer matrix:

- Three polymer matrices have been successfully synthesized, including *block copolymer* , *cross-linked block copolymer*, and *salt-added cross-linked polymer*
- The polyethylene oxide (PEO) cross-linked polymer exhibits an ionic conductivity of 2.40×10^{-4} S/cm at room temperature
- The plastic crystal-added solid polymer electrolytes exhibits ionic conductivity of 8.3×10^{-4} S/cm (in Yr3)

For inorganic nanofibers:

- $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) nanofibers and $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (LLTO) nanofibers have been developed.
- 0.5% Al-doped $\text{Li}_{0.33}\text{La}_{0.56}\text{Ti}_{0.995}\text{Al}_{0.005}\text{O}_3$ (LLATO) nanofibers exhibits ionic conductivity of 1.08×10^{-3} S/cm.

Milestones in Year 2-(10/01/2017– 10/31/2018)

For composite electrolyte:

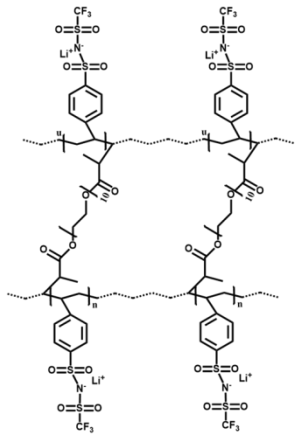
- A composite electrolyte consisting of silane-grafted $\text{Li}_{6.28}\text{La}_3\text{Al}_{0.24}\text{Zr}_2\text{O}_{12}$ (s@LLAZO) nanofibers and poly(ethylene glycol) diacrylate (PEGDA) monomer has been developed, showing an ionic conductivity of 4.9×10^{-4} S/cm.
- A composite electrolyte consisting of Li_3PO_4 -modified LLATO nanofibers and poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has been developed, showing an ionic conductivity of 5.1×10^{-4} S/cm.

Milestones in Year-3 (10/01/2018– Present)

Half cells and full cells:

- We have constructed and tested the batteries with silane-LLAZO incorporated cross-linked polymer composite as electrolyte, Li metal anode and LiFePO_4 (LFP) as cathode.
- We have constructed and tested the batteries with Li_3PO_4 -coated LLATO/PVDF-HFP composite as electrolyte, Li metal anode and LiFePO_4 (LFP) as cathode.
- We have constructed and tested the batteries with flexible carbon nanofiber (CNF)/S-PEO/LLTO bilayer as cathode-electrolyte bilayer structure for room-temperature all-solid-state lithium-sulfur batteries.

Approach



- Design and engineer the polymer matrix

Develop the block copolymers or cross-linked polymers that have higher ionic conductivity than traditional polyethylene oxide (PEO) polymers.

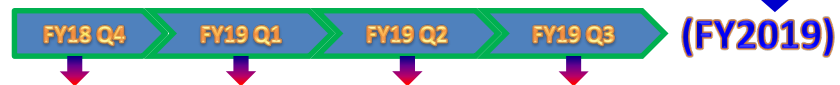
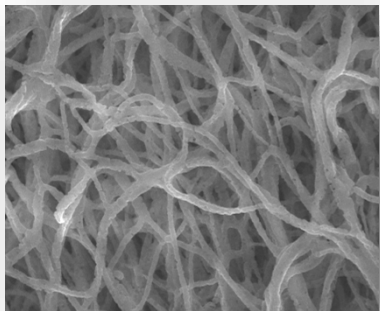
Approach identified to optimize ion-conducting polymers and inorganic nanofibers.



- Design and engineer the inorganic nanofibers

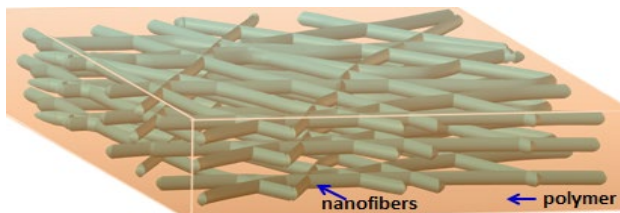
- Provide continuous Li⁺ transport channels via nanofiber network
- Inhibit crystallization of amorphous polymer electrolyte.
- Facilitate lithium salt dissociation and ion transport through the polymer electrolyte

Approach identified to optimize development composite electrolytes.



- Enhance the synergistic effect of integrated inorganic fiber-polymer composites

- In-situ polymerization
- Design linker to couple the nanofibers to the polymer matrix
- Design deliberately to suppress the formation of lithium dendrites
- Measure the mechanical and electrochemical properties of composites
- Optimize the nanofiber-polymer composites



Approach

Innovation

Polymer matrix:

- Compared with the complicate synthesis procedures reported before, such as ring opening polymerization, our cross-linked acrylate-based PEO polymers are fabricated through easy UV cross-linking process.
- Compared with the crystalline PEO structure, ours has fully amorphous PEO structure.
- Compared with previous double cross-linkers with high T_g (-20°C), our polymer is plasticized with PEG, showing low glass transition temperature T_g (-56.5°C).
- Compared with the low ionic conductivity of the previous PEO based polymers (10^{-9} - 10^{-6} S/cm), ours has higher ionic conductivity, for example the salt-added cross-linked polymer can reach an ionic conductivity of 2.4×10^{-4} S/cm.

Inorganic nanofibers:

- Hydrogen-treatment is performed to create oxygen vacancies in Li-conducting metal oxides, showing improved ionic conductivity
- Li-conducting metal oxides are doped with anions (nitrogen) while cation doping is reported in previous studies. Nitrogen doping can create the stable oxygen vacancy in the metal oxides.

Ceramic-polymer composite electrolyte:

- Composite electrolytes are prepared with in-situ polymerization on the ceramic nanofiber network.
- Grating agent is introduced at the ceramic/polymer interface in the composite.
- The ceramic nanofibers are surface-modified with a high ionic conductivity buffer layer, which is located at the ceramic/polymer interface in the composite.

Full-cell batteries:

- All-solid-state Li-ion batteries are developed, which greatly improves the safety during operation.
- Use of solid-state electrolyte suppresses the dendrite formation.
- All-solid-state Li-ion batteries show excellent cycle-stability, including high capacity retention and high columbic efficiency

Technical Accomplishments and Progress

Work done in Year 3 (04/01/2018 ~ 03/31/2019):

Polymer matrix:

- Developed the plastic crystal-added solid polymer electrolytes
- Optimized the cross-linked PEGDA-LiTFSI polymer electrolyte

Ceramic-polymer composite electrolyte:

- Optimized the silane-LLAZO-cross-linked polymer composite electrolyte
- Optimized the lithium phosphate buffer layer the LLATO/polymer composite

Coin-cell batteries:

- Tested the cycling performance, Coulombic efficiency and charge/discharge curves of the Li|s@LLAZO(6h)-60PEGDA|LFP battery
- Tested the cycling performance, Coulombic efficiency and charge/discharge curves of the Li| PVDF-HFP/LiTFSI/LLATO/Li₃PO₄|LFP battery
- Tested the cycling performance, Coulombic efficiency and charge/discharge curves of the CNF/S-PEO/LLTO bilayer framework based Li –S battery

Current Progress in:

Polymer Matrix

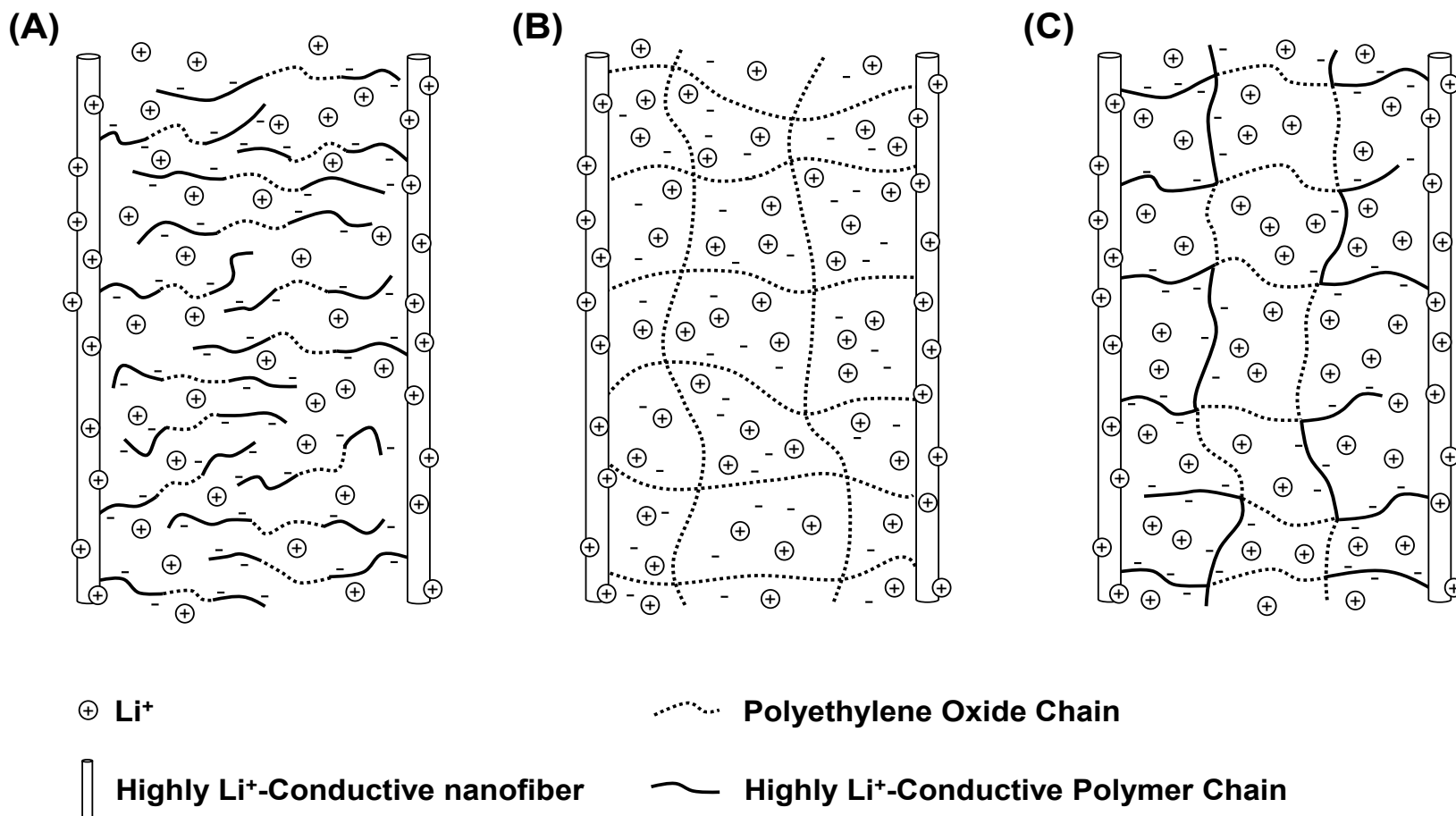
- ◉ Plastic crystal-added solid polymer electrolytes
- ◉ Cross-linked PEGDA-LiTFSI polymer electrolyte

Development of new Li ion-conducting polymers

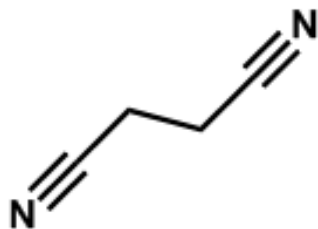
A: Block co-polymer formation

B: Cross-linking

C: Combination of block co-polymer formation and cross-linking



Plastic crystal-added solid polymer electrolytes



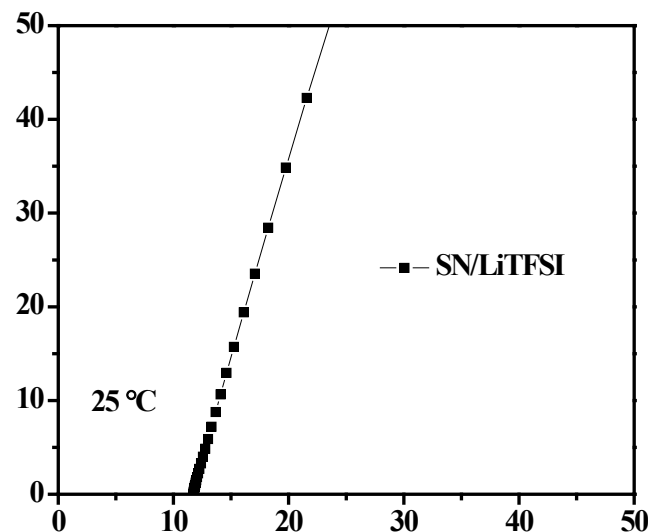
Succinonitrile

Plastic crystals

- Increase structure disorder
- Enhance diffusivity in polymer electrolytes

Succinonitrile (SN)

- Plastic crystals
- Nitrile groups ($-\text{C}\equiv\text{N}$) comprise good solvation capability
- Strong interaction with Li



Solid electrolyte (SN/LiTFSI)

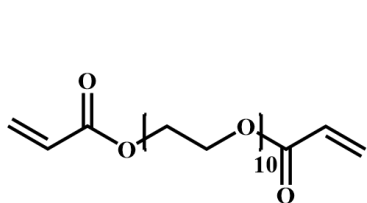
- $[\text{SN}]/[\text{Li}^+]$ of 10:1
- High ionic conductivity of $2.1 \times 10^{-3} \text{ S cm}^{-1}$

Problems (when polymer is not present)

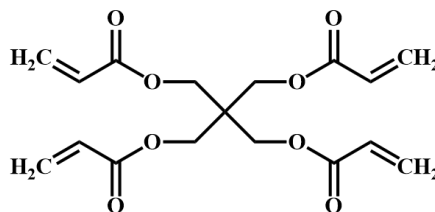
- × No self-standing film
- × Extremely plastic
- × Susceptible to deformation under external

stress

Plastic crystal-added solid polymer electrolytes



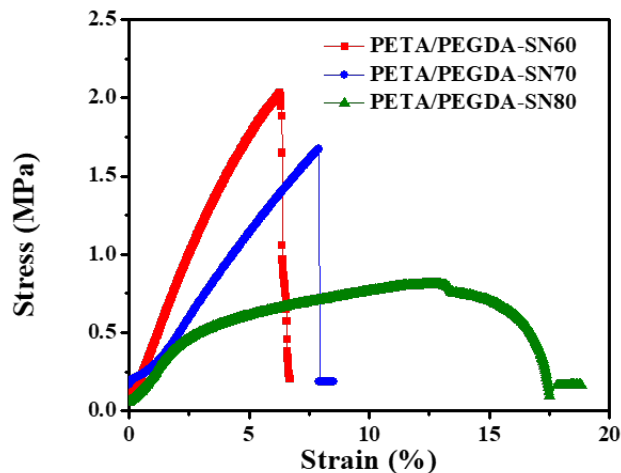
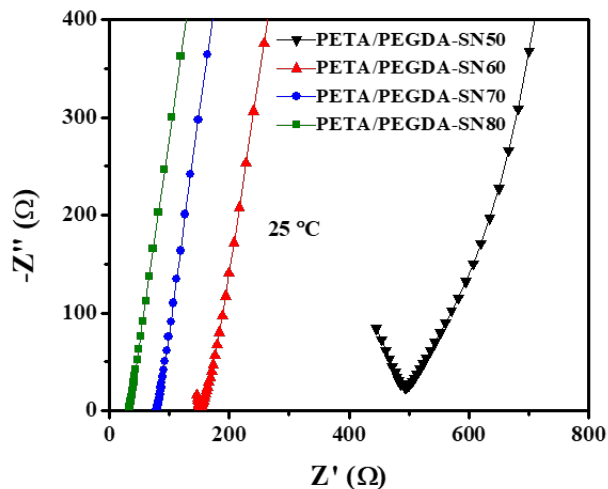
Poly(ethylene glycol) diacrylate
(PEGDA)



Pentaerythritol tetraacrylate
(PETA)

Robust and mechanically strong polymer framework

- PEGDA+PETA (50:50, wt.%)
- High modulus, 44.65 MPa

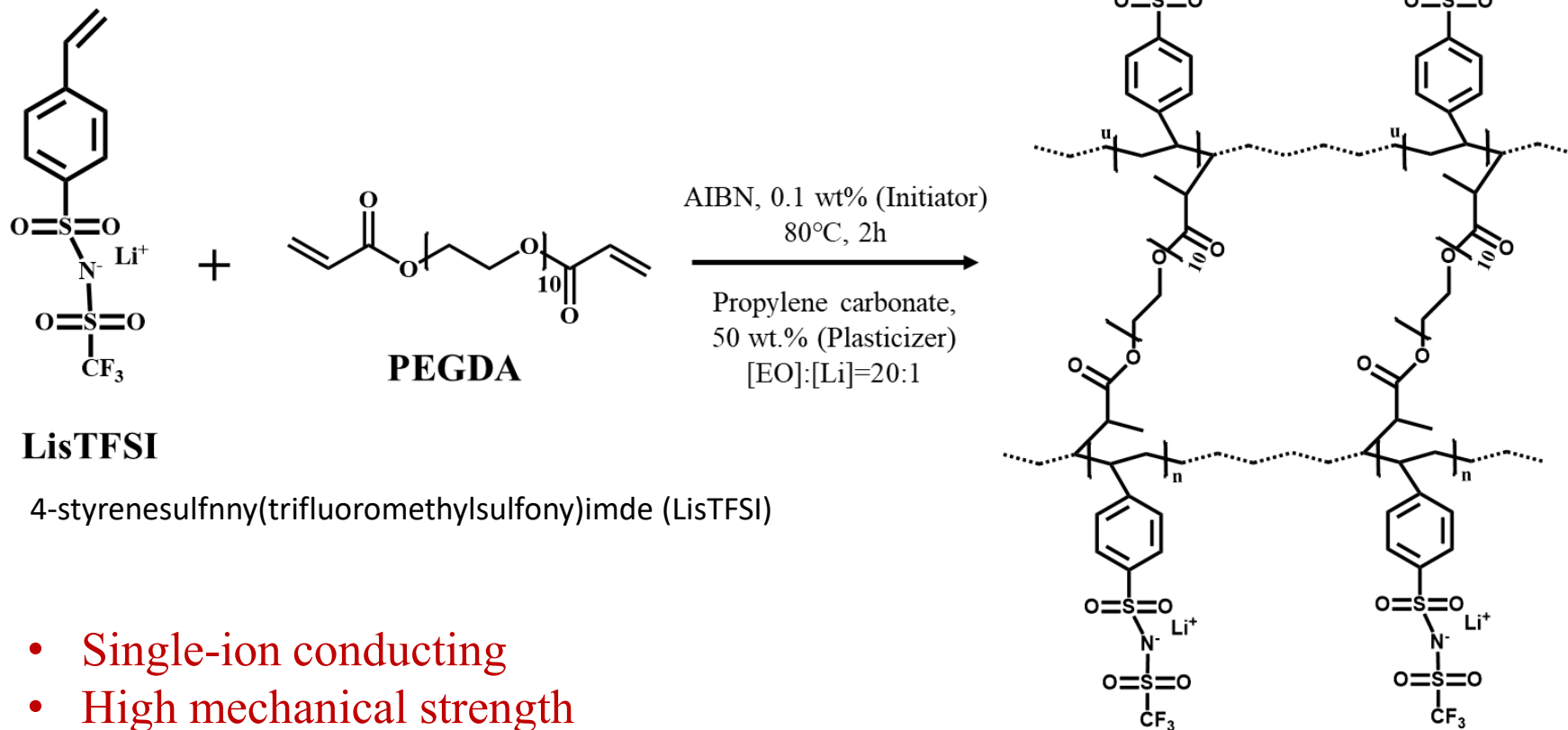


Samples	SN content (%)	Ionic Conductivity (S/cm) (at 25 °C)	Young's modulus (MPa)
PETA/PEGDA-SN50	50	3.9×10^{-5}	-
PETA/PEGDA-SN60	60	9.7×10^{-5}	36.7
PETA/PEGDA-SN70	70	3.4×10^{-4}	20.1
PETA/PEGDA-SN80	80	8.3×10^{-4}	7.3

Polymer 2:

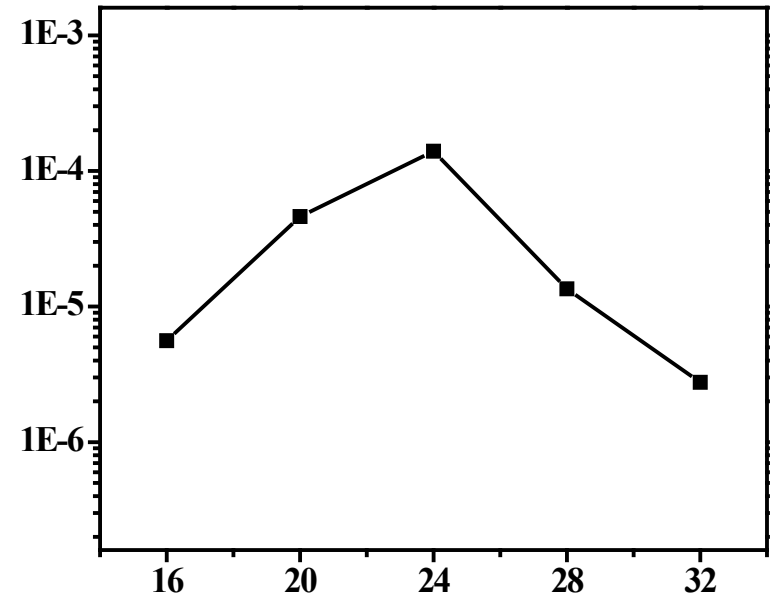
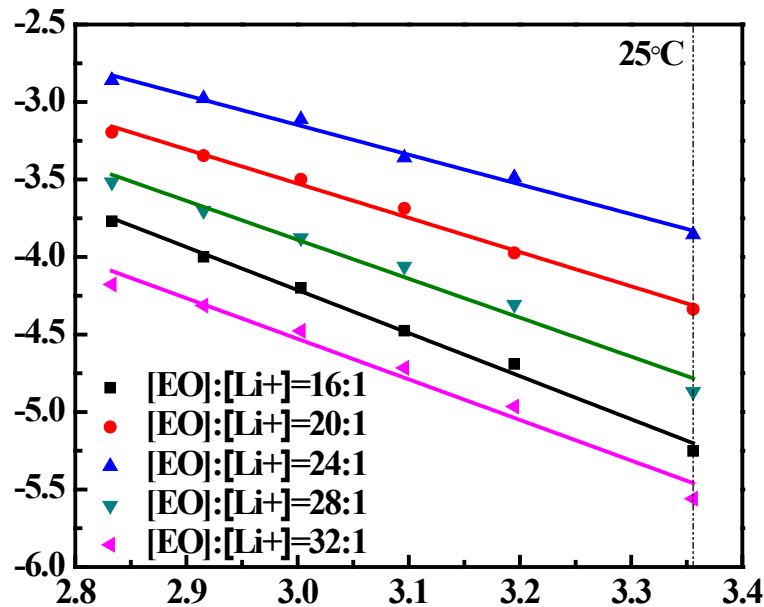
Cross-linked PEGDA-LisTFSI polymer electrolyte

- Synthesis procedure:



- Single-ion conducting
- High mechanical strength
 - Lithium blocks have high rigidity

Cross-linked PEGDA-LisTFSI polymer electrolyte

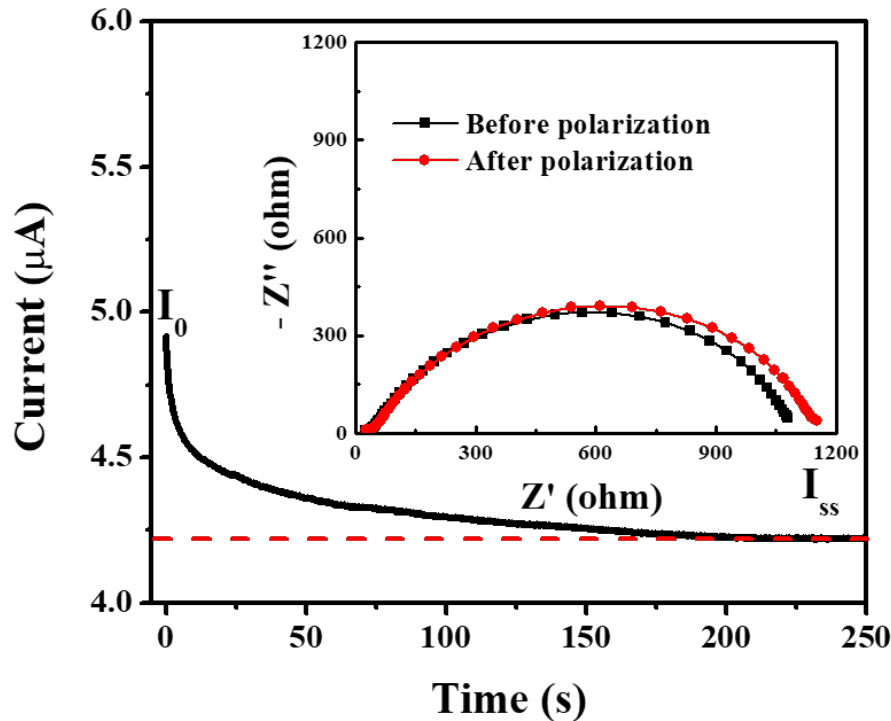


High ionic conductivity after plasticized with propylene carbonate (PC)

- 50 wt.% PC added based on the weight of PEGDA-LisTFSI
- [EO]:[Li⁺] = 24:1, highest ionic conductivity ($1.5 \times 10^{-4} \text{ S cm}^{-1}$)

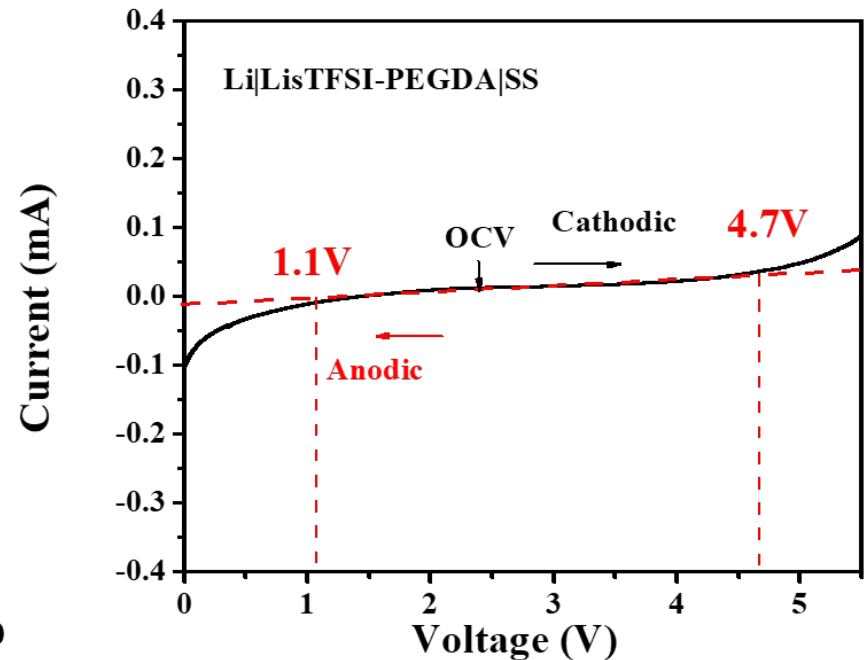
Polymer 2:

Cross-linked PEGDA-LiTFSI polymer electrolyte



Single-ion conductor

- $t_{\text{Li}^+} = 0.82$



Electrochemical window

- 1.1 V ~ 4.7 V

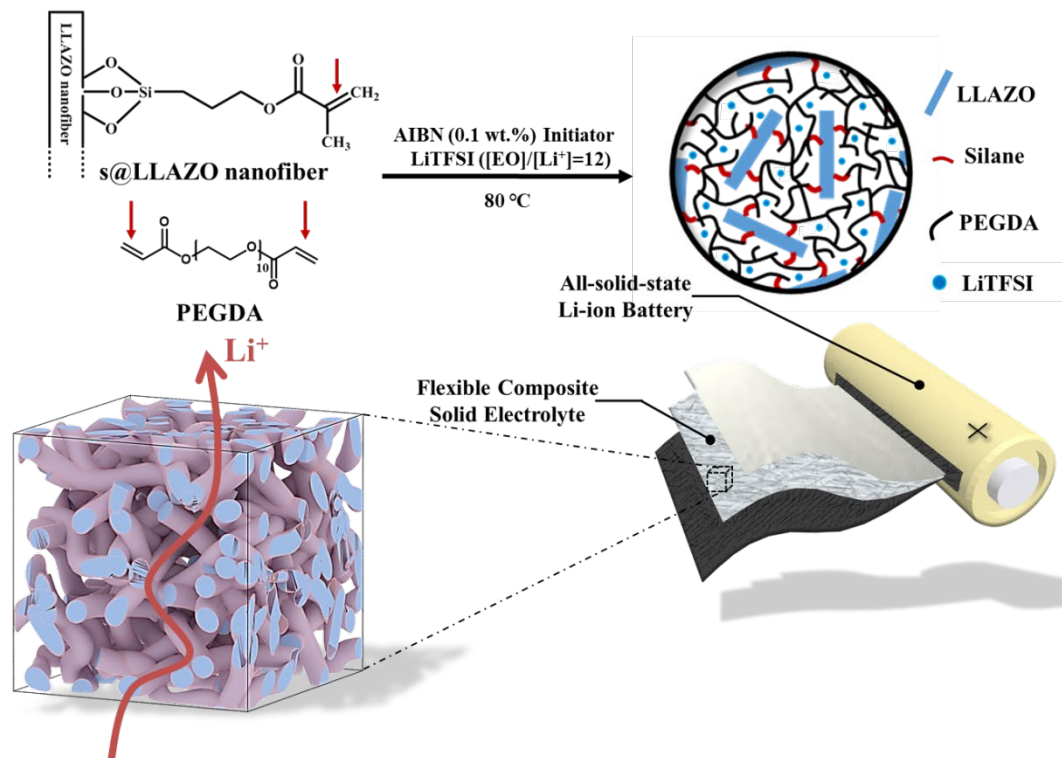
Current Progress in:

Nanofiber-Polymer Composite Electrolytes

- ◉ Silane-LLAZO incorporated cross-linked polymer composite electrolyte
- ◉ Li_3PO_4 coated Al-doped LLTO solid electrolyte for all-solid-state lithium batteries (PVDF-HFP/LiTFSI/LLATO/ Li_3PO_4)

Composite solid electrolyte 1:

Silane-LLAZO incorporated cross-linked polymer composite electrolyte



Roles of silane grating agent:

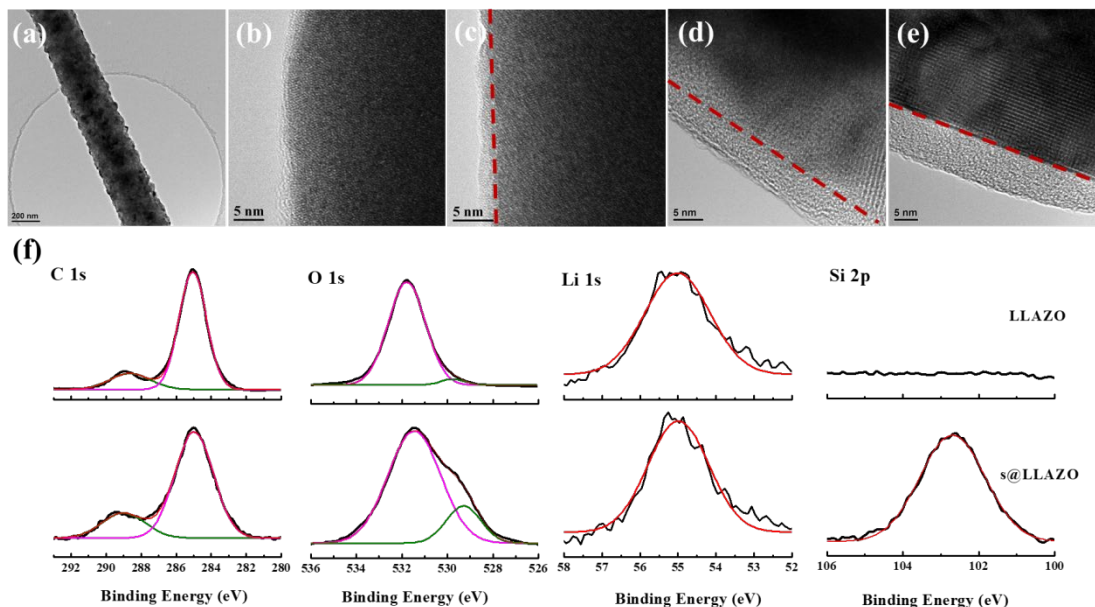
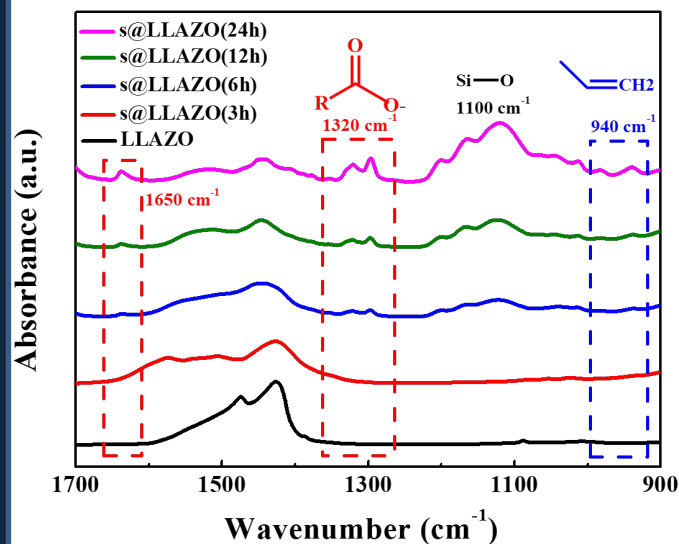
- Decrease interfacial resistance between filler and polymer
- Lower polymer content used in the solid electrolyte (40 wt.%)
- Control the fabrication composite framework (percolated network)
- High ionic conductivity
- High lithium transference number

Synthesis process

- Silane coating (s@LLAZO nanofibers)
 - 2.5 wt% 3-(trimethoxysilyl)propyl methacrylate (Silane) in ethanol/H₂O (95:5 volume ratio) for 6h
- Polymerization (composite solid electrolyte)
 - 40 wt% poly(ethylene glycol) dimethyl acrylate (PEGDA) + LiTFSI
 - 60 wt% s@LLAZO nanofibers

Composite solid electrolyte 1: Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Structural Characterization

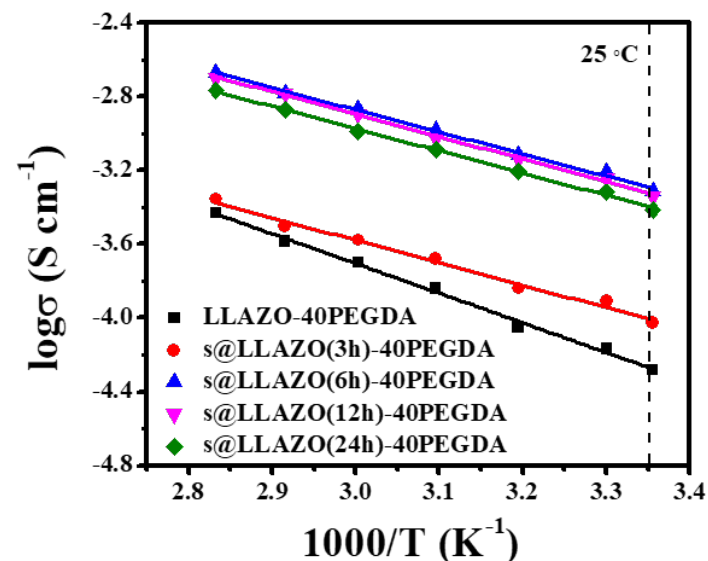
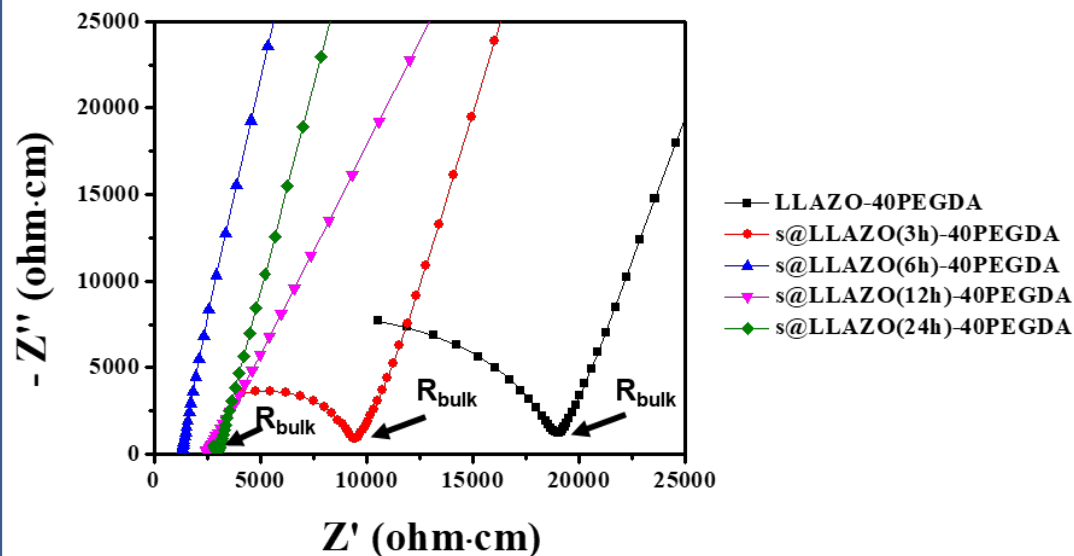


- Silane is successfully grafted onto the surface of LLAZO nanofibers
 - Si-O groups, C=C groups, acrylate groups appear in FTIR
- Coating layer thickness increases along with the increased treatment time
- XPS surface functional groups (Si-O groups)
 - O 1s at 531.5 eV, Si 2p at 102.5 eV

Composite solid electrolyte 1:

Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Electrochemical Characterization



Samples	Silane Coating Time (h)	Ionic Conductivity (S/cm) (at 25 °C)	Activation Energy (eV)
LLAZO-PEGDA	0	5.2×10^{-5}	0.41
s@LLAZO(3h)-40PEGDA	3	9.4×10^{-5}	0.31
s@LLAZO(6h)-40PEGDA	6	4.9×10^{-4}	0.29
s@LLAZO(12h)-40PEGDA	12	4.6×10^{-4}	0.30
s@LLAZO(24h)-40PEGDA	24	3.9×10^{-4}	0.30

s@LLAZO(6h)-PEGDA

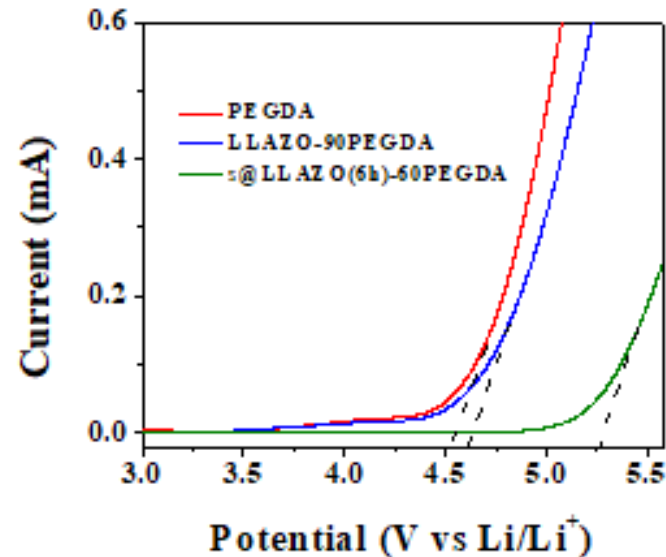
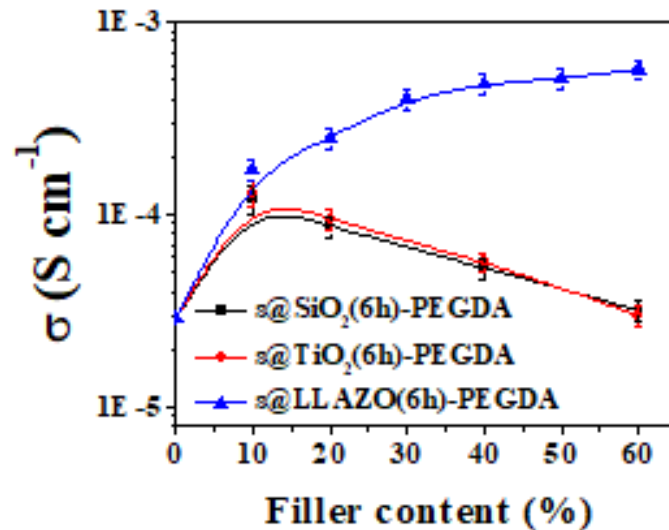
- Highest ionic conductivity
- Optimum silane coating

Different Li⁺ conduction preference (E_a)

- Polymer matrix (LLAZO-PEGDA)
High activation energy
- Percolated LLAZO nanofiber (s@LLAZO-PEGDA)
Low activation energy

Composite solid electrolyte 1: Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Electrochemical Characterization



Fit well with percolation model

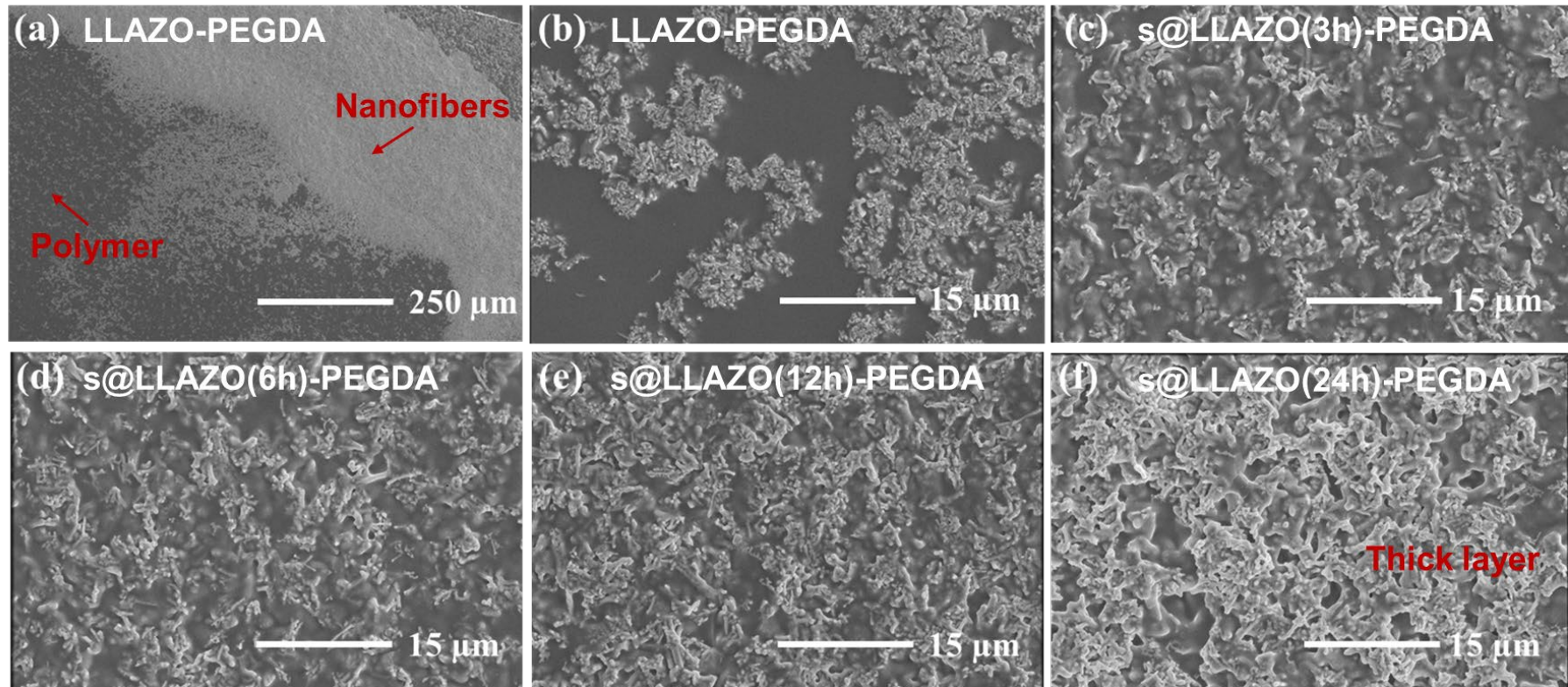
- σ Increases continuously
- eliminate agglomeration effect

Silane-coated non- Li^+ conductor

- $\text{s@TiO}_2(6\text{h})$, $\text{s@SiO}_2(6\text{h})$
- σ greatly decreases after 10wt.%

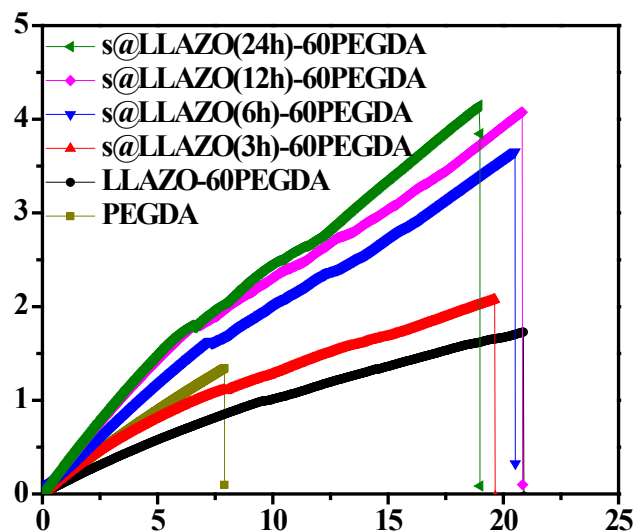
s@LLAZO filler provides significant contribution to Li^+ ion conduction

Morphologies of composite solid electrolytes



- **LLAZO-PEGDA composite solid electrolyte**
 - Severe aggregation of nanofibers (discontinued Li^+ conduction)
- **s@LLAZO-PEGDA composite solid electrolytes**
 - Well percolated LLAZO network (continuous Li^+ conduction)

Mechanical properties

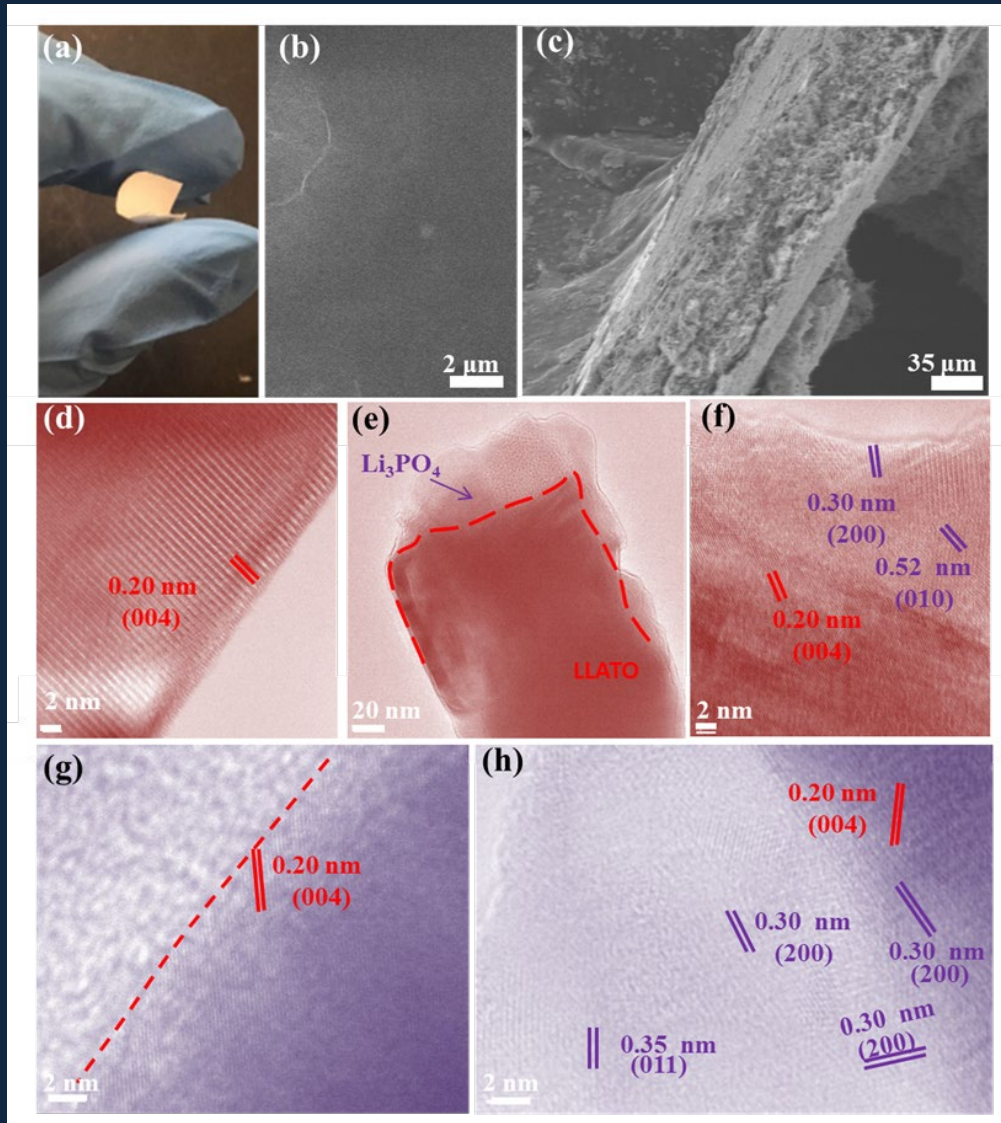


Samples	Silane Coating Time (h)	Young's modulus (MPa)	Tensile Strength (MPa)
LLAZO-PEGDA	0	10.4	1.7
<u>s@LLAZO(3h)-40PEGDA</u>	3	17.8	2.1
<u>s@LLAZO(6h)-40PEGDA</u>	6	24.8	3.7
<u>s@LLAZO(12h)-40PEGDA</u>	12	27.6	4.1
<u>s@LLAZO(24h)-40PEGDA</u>	24	29.5	4.2

Composite solid electrolyte 2:

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

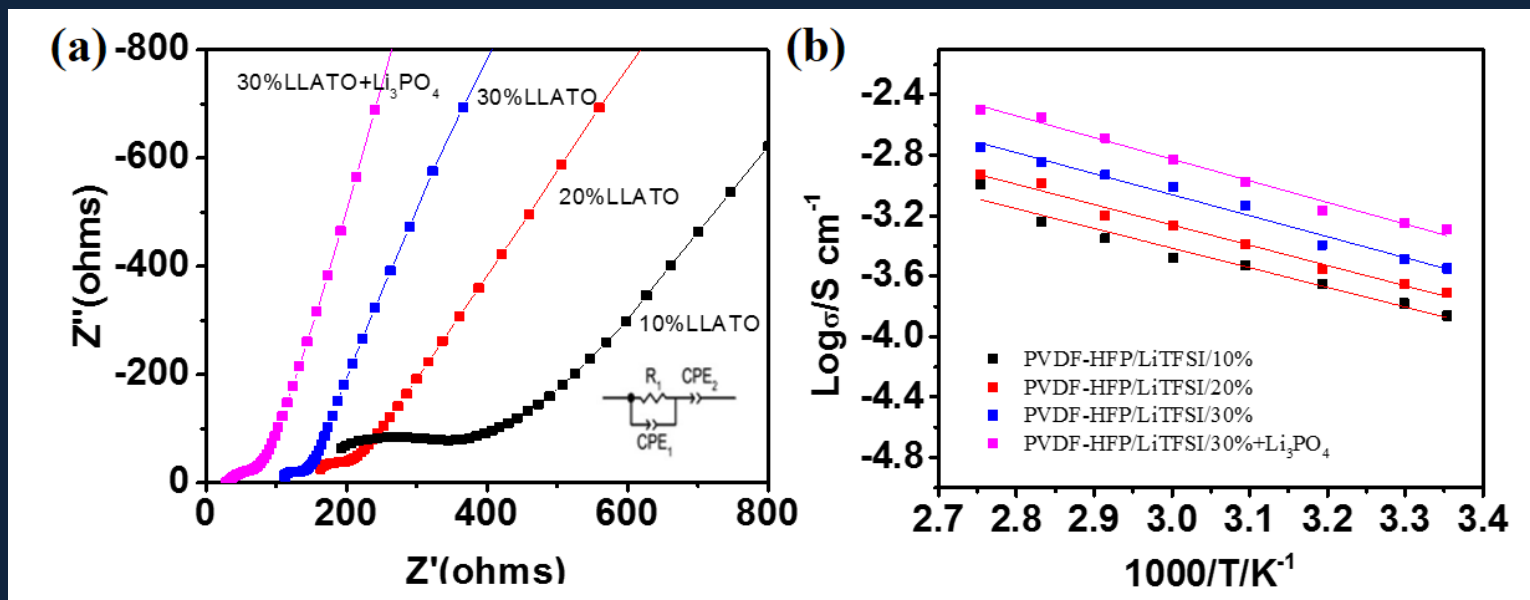
Morphology of composite electrolyte



- The electrolyte shows good flexibility which can be used to construct flexible solid-state lithium batteries
- The thickness of composite electrolyte is about $\sim 80 \mu\text{m}$
- A thin lithium phosphate film has covered after the surface modification as shown in Figure e and f, forming a LLATO core/ Li_3PO_4 shell structure
- Interface between polymer matrix and nanofibers
 - PVDF-HFP/LiTFSI/LLATO: sharp
 - PVDF-HFP/LiTFSI/LLATO/ Li_3PO_4 : gradually

Li₃PO₄-coated LLATO/PVDF-HFP/LiTFSI composite

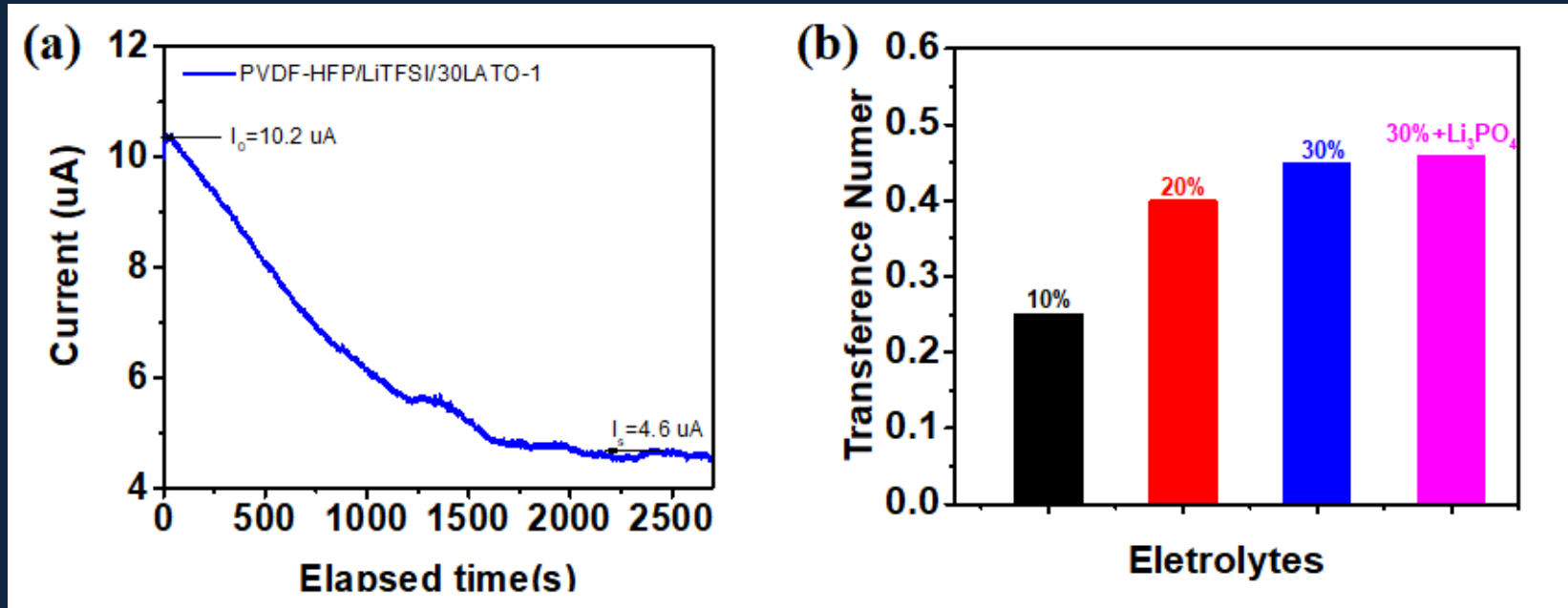
Ionic conductivity of composite electrolyte



Samples	Nanofiber amount (%)	Ionic Conductivity (S/cm) (at 25 °C)	Activation Energy (eV)
PVDF-HFP/ <u>LiTFSI</u> /LLATO(10)	10	1.7×10^{-4}	0.25
PVDF-HFP/ <u>LiTFSI</u> /LLATO(20)	20	2.4×10^{-4}	0.23
PVDF-HFP/ <u>LiTFSI</u> /LLATO(30)	30	4.0×10^{-4}	0.23
PVDF-HFP/ <u>LiTFSI</u> /LLATO(30)/Li ₃ PO ₄	30+Li ₃ PO ₄	5.1×10^{-4}	0.22

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

Li^+ ion transference number



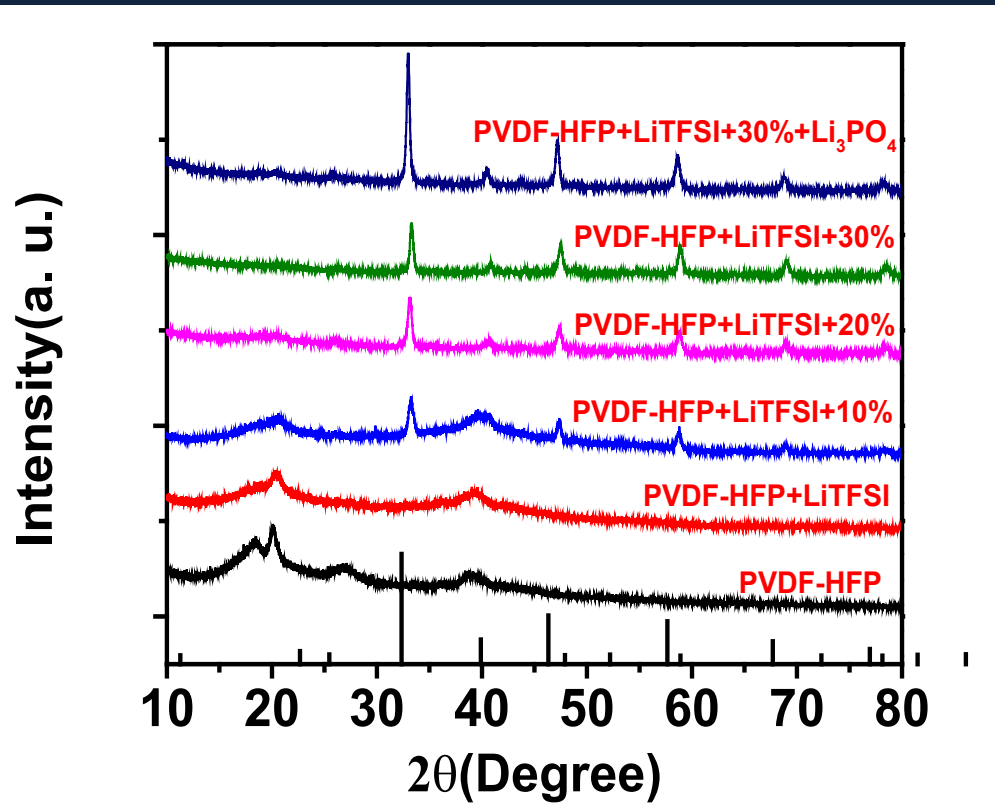
Li^+ ion transference number

- Chronoamperometry profiles in Li/SEs/Li with an applied DC voltage of 10 mV
- Higher nanofibers amount, faster Li^+ ion conduction

Composite solid electrolyte 2:

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

XRD patterns of composite electrolyte



PVDF-HFP alone shows characteristic peaks at 18, 20, 27, 40°

Adding lithium salt LiTFSI:

- weakened the XRD diffraction peaks of PVDF-HFP

Adding ceramic nanofibers

- further weakened the diffraction peaks of PVDF-HFP

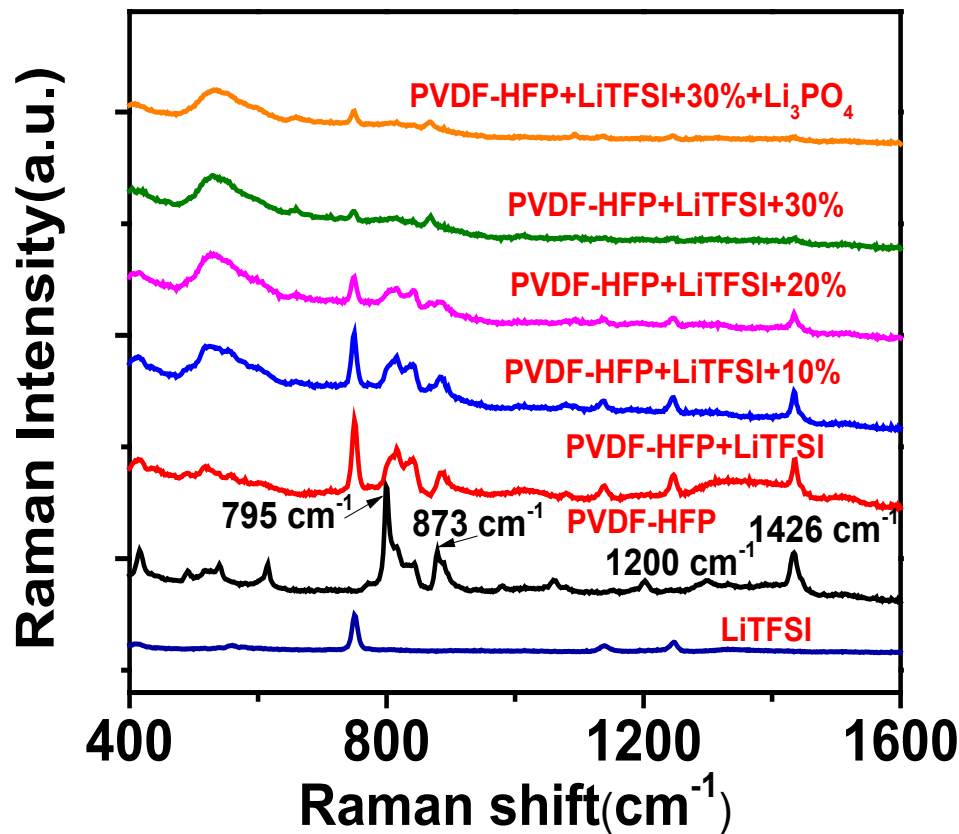
More amorphous regions were formed in the PVDF-HFP polymer matrix with increasing the content of LLATO nanofibers

Composite solid electrolyte 2:

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

Raman spectra of composite electrolyte

Adding lithium salt LiTFSI:

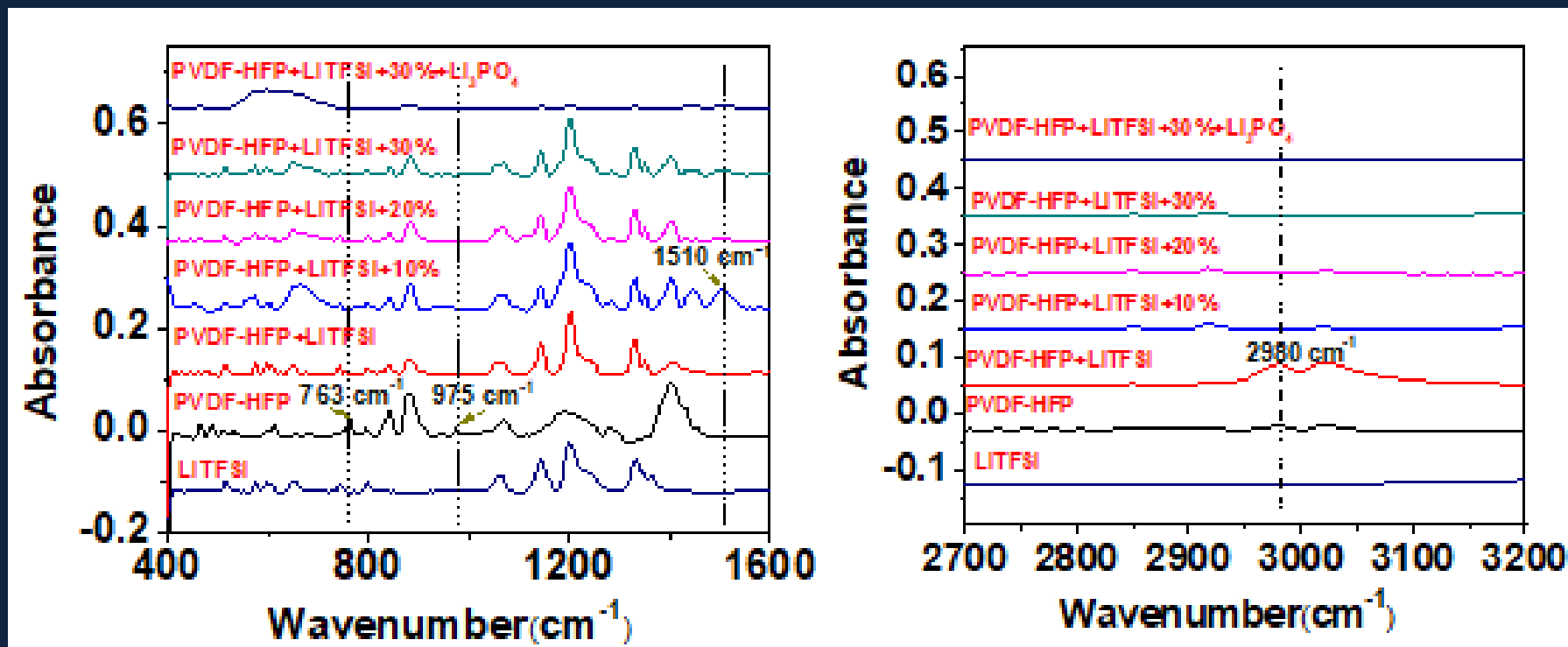


- deprotonation of CH_2
 - peaks at 795 cm^{-1} , 873 cm^{-1} and 1426 cm^{-1} decreased
- weakened α phase of PVDF-HFP
- dehydrofluorination of PVDF-HFP chains
 - CF_2 stretching vibration mode at 1200 cm^{-1} of PVDF-HFP decreased dramatically

Composite solid electrolyte 2:

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

FTIR spectra of composite electrolyte

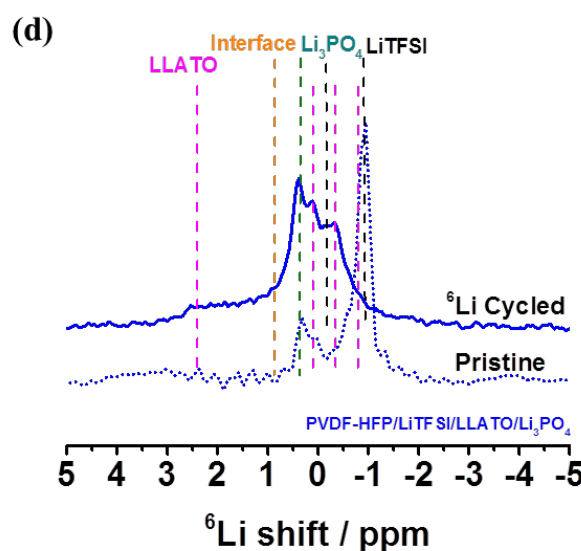
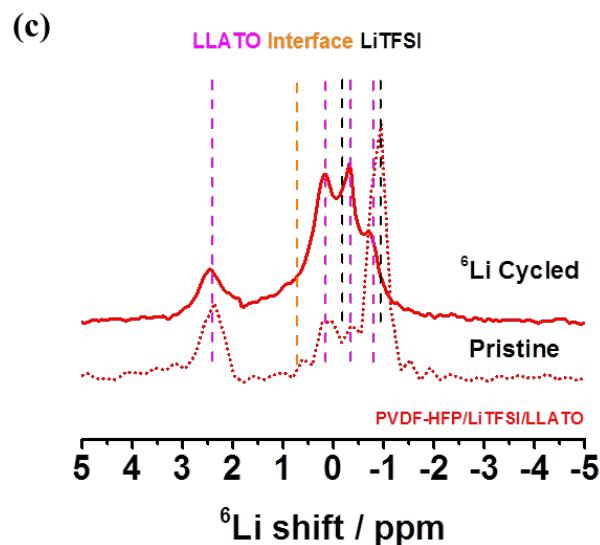
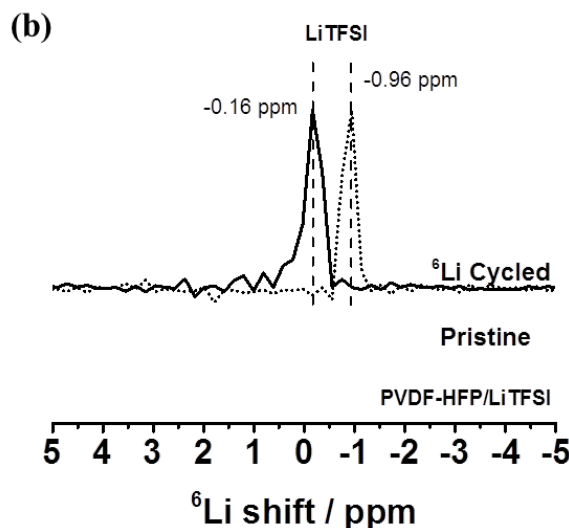
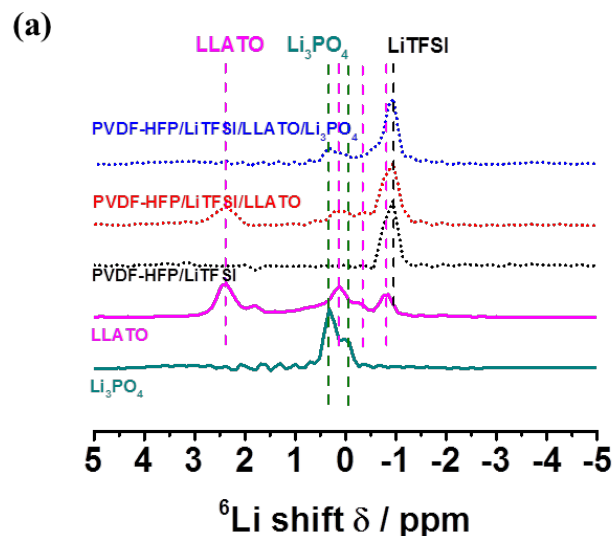


Adding ceramic nanofibers:

- deprotonation of CH_2
 - CH_2 stretching mode peak at 2980 cm^{-1} almost disappeared
- dehydrofluorination of PVDF chains
 - A new peak at 1510 cm^{-1} , the C=C stretching modes of polyene

Li₃PO₄-coated LLATO/PVDF-HFP/LiTFSI composite

Li⁺ ion transport pathway analysis with ⁶Li ssNMR:



Reference:

LiTFSI in the PVDF-HFP/LiTFSI : -0.96 ppm.
Pure LLATO : -0.81, -0.25, 0.13, 1.8, and 2.4 ppm.
pure Li₃PO₄: 0.33 ppm, 0 ppm

Before vs. After ⁶Li → ⁷Li replacement:

1). PVDF-HFP/LiTFSI:
LiTFSI shift: -0.96 ppm to -0.16 ppm,

2). PVDF HFP/LiTFSI/LLATO:
LLATO shift: -0.30, and 0.13ppm shifted to -0.33, and 0.19 ppm , and increased significantly after 6Li → 7Li replacement.

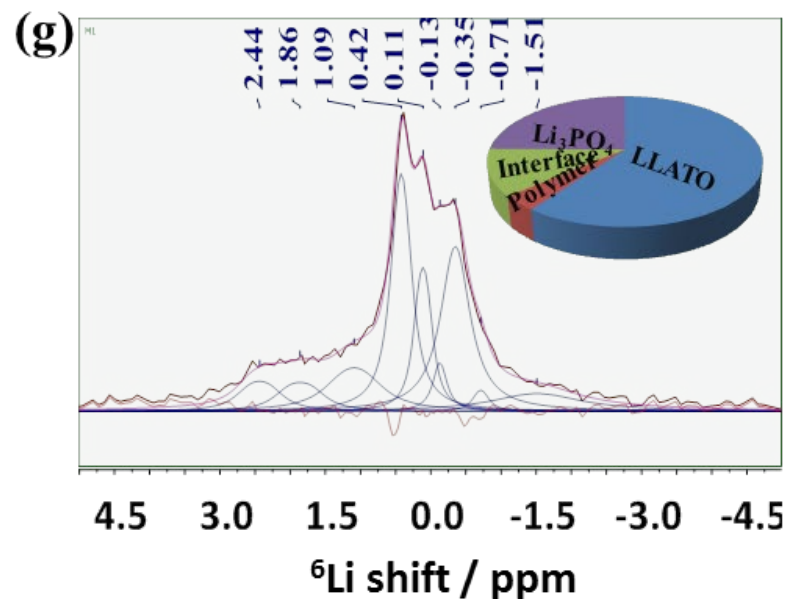
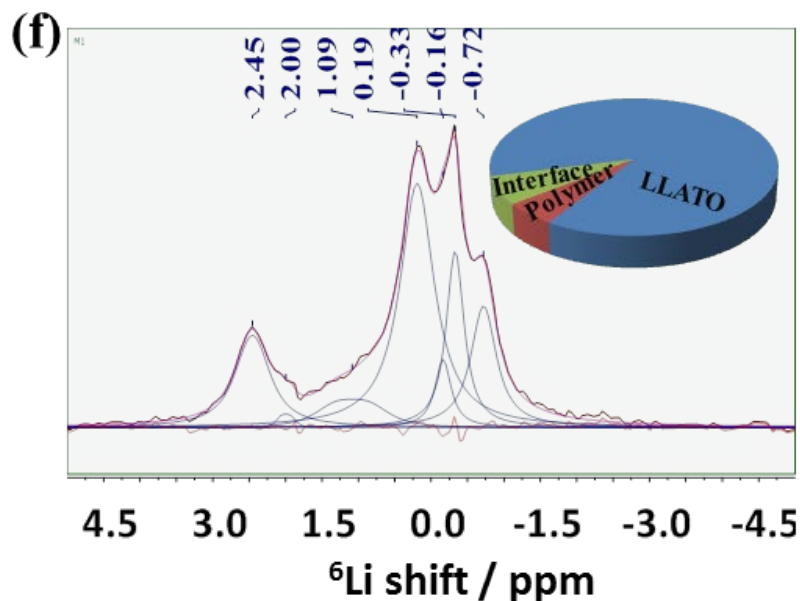
The majority of Li ions pass through the percolated network formed by LLATO nanofibers and a small portion transport via LiTFSI in PVDF-HFP and the interface.

3). PVDF-HFP/LiTFSI/LLATO/Li₃PO₄:
LLATO shift: -0.30, and 0.13ppm shifted to -0.34, and 0.12ppm, and increased significantly after 6Li → 7Li replacement.
Li₃PO₄: 0.33 ppm to 0.42 ppm, increased dramatically after the 6Li → 7Li replacement.

Li_3PO_4 -coated LLATO/PVDF-HFP/LiTFSI composite

Li^+ ion transport pathway analysis with ^6Li ssNMR:

spectral simulation, assignments, and quantification results



PVDF-HFP/LiTFSI/LLATO:

Li^+ from LLATO nanofibers: 87.9 mol %
 Li^+ from LiTFSI: 5.4 mol %
 Li^+ from the interface: 6.7 mol %

PVDF-HFP/LiTFSI/LLATO/ Li_3PO_4 :

Li^+ from LLATO nanofibers: 60 mol %
 Li^+ from LiTFSI: 3.7 mol %
 Li^+ from the interface: 11.5 mol %
 Li^+ from interfacial Li_3PO_4 : 24.8 mol %

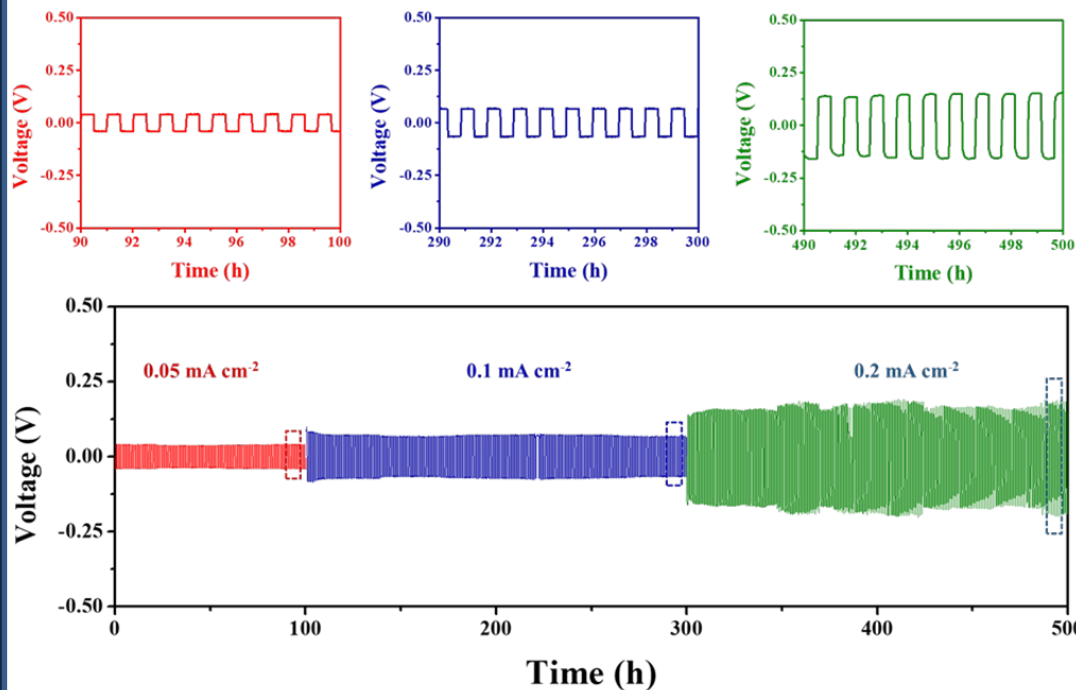
The modification of the Li_3PO_4 buffer layer improved the Li^+ ion transport at the interface.

Current Progress in:

COIN-CELL BATTERY

Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Half Cells



Excellent mechanical properties

- Bendable, rolled up without crack

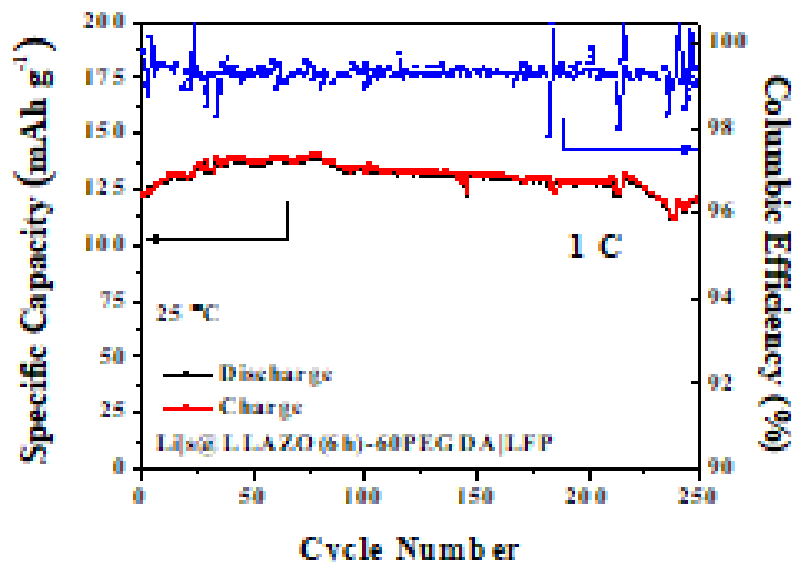
Long-term lithium cycling stability

- Low overpotentials
 - 35 mV @ 0.05 mA cm⁻²
 - 69 mV @ 0.1 mA cm⁻²
 - 159 mV @ 0.2 mA cm⁻²
- Smooth Li stripping/plating
 - Over 500 hours

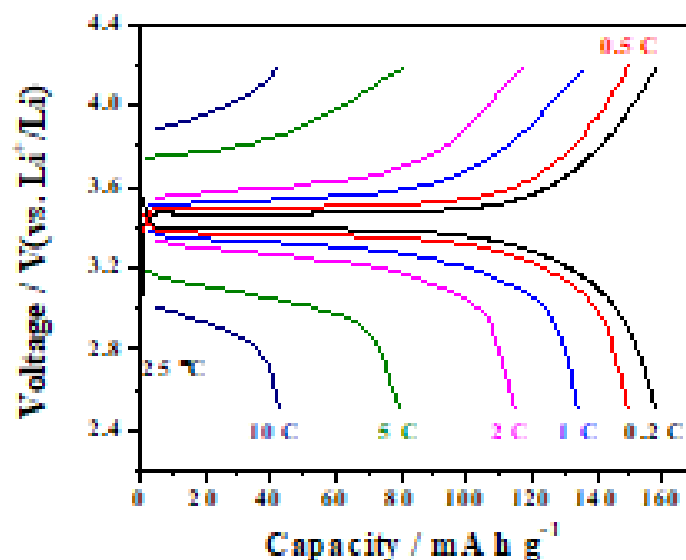
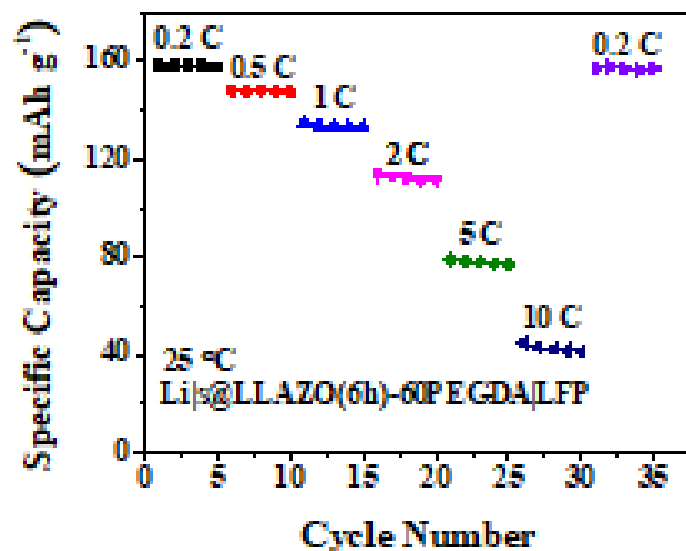
Stable interface between Li metal and s@LLAZO-PEGDA CSE

Silane-LLAZO incorporated cross-linked polymer composite electrolyte

Li/composite electrolyte/LFP Full Cells: Cycling performance & rate capacity:

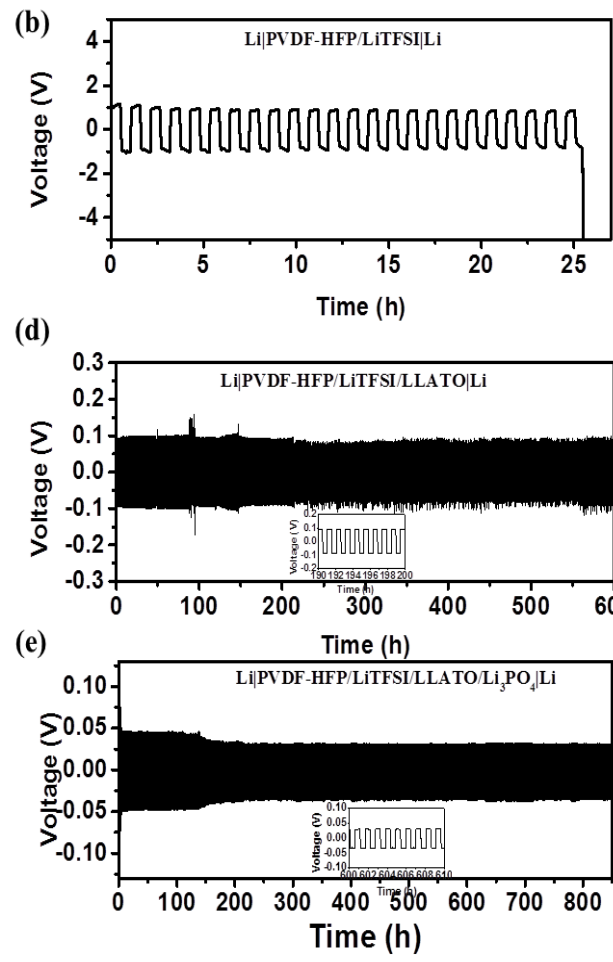
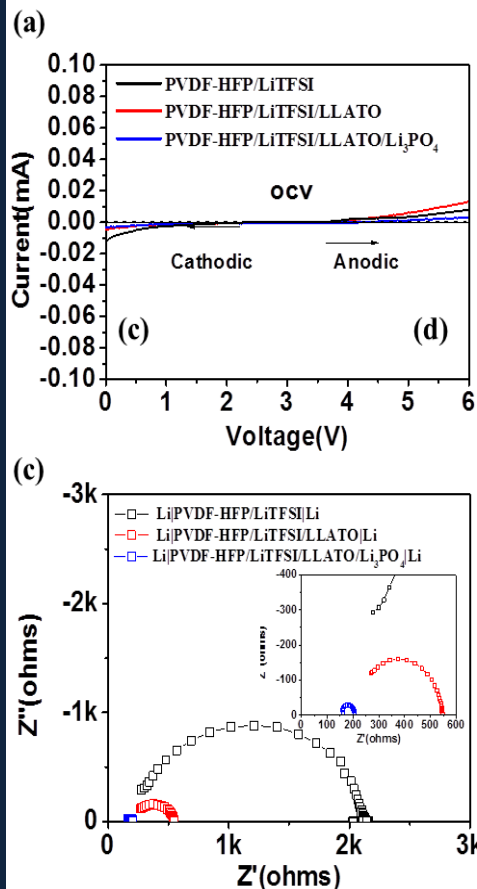


- Stable cycling performance @1C
 - 115 mAh g⁻¹ up to 250 cycles
 - 89% capacity retention
 - 99% Coulombic efficiency
- Remarkable rate capability
 - 113 mAh g⁻¹ @ 2C
 - 78 mAh g⁻¹ @ 5C
 - Working up to 10C (44 mAh g⁻¹)
- Good reversibility of the redox reactions
 - Superior electrochemical properties of CSE



Li₃PO₄-coated LLATO/PVDF-HFP composite

Half Cells



PVDF-HFP/LiTFSI:

- failed after 25 cycles
- polarization voltages of ~1 V were observed at 0.5 mA/cm² for 30 min at room temperature

PVDF-HFP/LiTFSI/LLATO:

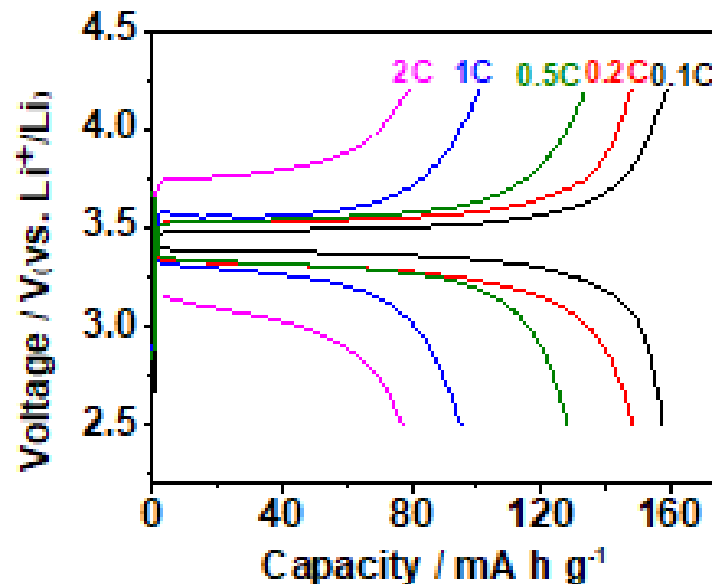
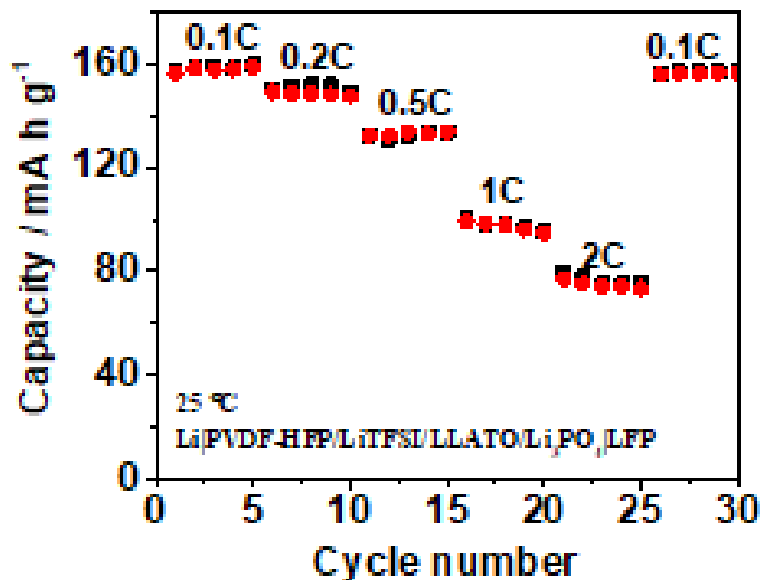
- polarization voltages of ~100 mV were observed at 0.5 mA/cm² for 30 min at room temperature

PVDF-HFP/LiTFSI/LLATO/Li₃PO₄:

- Charge/discharge at constant current densities
- Small polarization voltages of <50 mV were observed at 0.5 mA/cm² for 30 min at room temperature after 850 h of cycling

Li₃PO₄-coated LLATO/PVDF-HFP composite

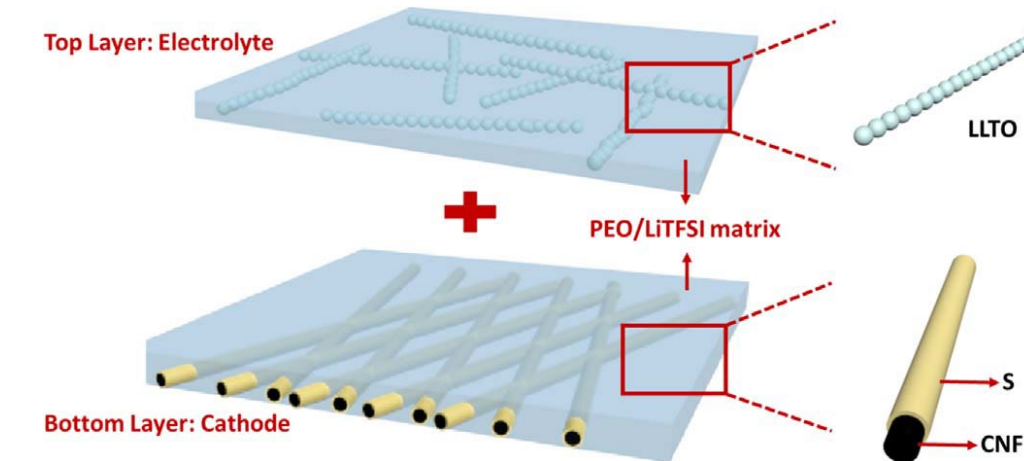
Li/composite electrolyte/LFP Full Cells: Cycling performance & rate capacity:



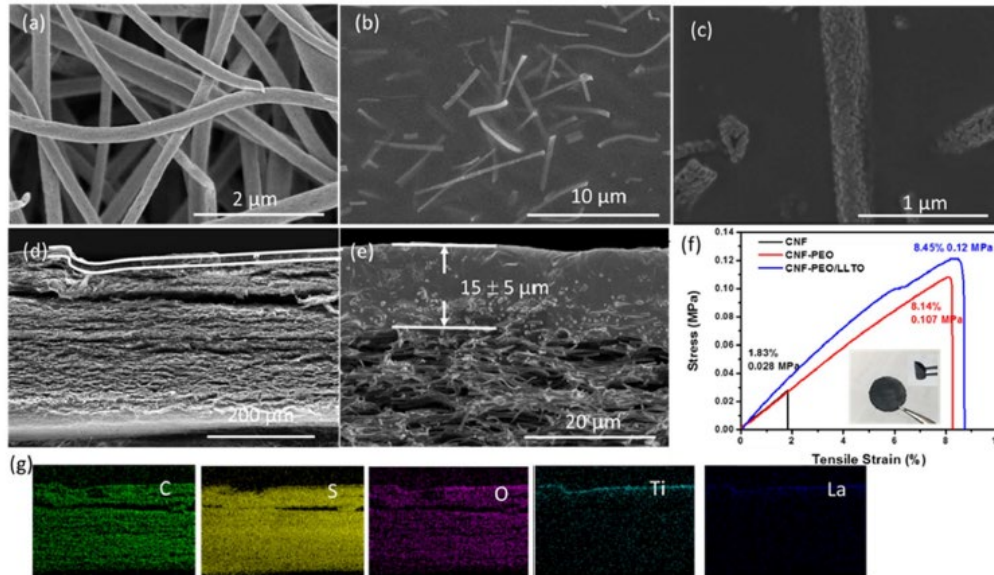
- Synergy of polymer matrix and nanofibers
 - High Li⁺ conductivity
 - Good mechanical properties
- Good rate capability: 0.1C (158 mAh/g), 0.2C (147 mAh/g), 0.5C (133 mAh/g), 1C (98 mAh/g), 2C (76 mAh/g).

Flexible CNF/S-PEO/LLTO bilayer structure bilayer framework

Fabrication and characterization of CNF/S-PEO/LLTO bilayer structure:



- The bilayer structure was prepared by direct casting PEO/LLTO solution onto the carbon nanofiber (CNF)/S cathode
- The CNF/S electrode was prepared by dropping a mixed liquid solution of S/carbon disulfide (S/CS₂) onto the CNF mat, ensuring the intimate contact between the active material (S) and the current collector (CNF mat).



(a) SEM images of CNF/S, and (b) PEO/LLTO solid composite electrolyte.

(c) High resolution SEM image of PEO/LLTO solid composite electrolyte with clearly seen LLTO structure.

(d) (e) Cross-sectional SEM image of CNF/S-PEO/LLTO bilayer framework

(f) Stress-strain curves of CNF, CNF-PEO and CNF-PEO/LLTO

(g) EDS mapping of the cross-section of CNF/S-PEO/LLTO bilayer framework (e).

Flexible CNF/S-PEO/LLTO bilayer structure bilayer framework

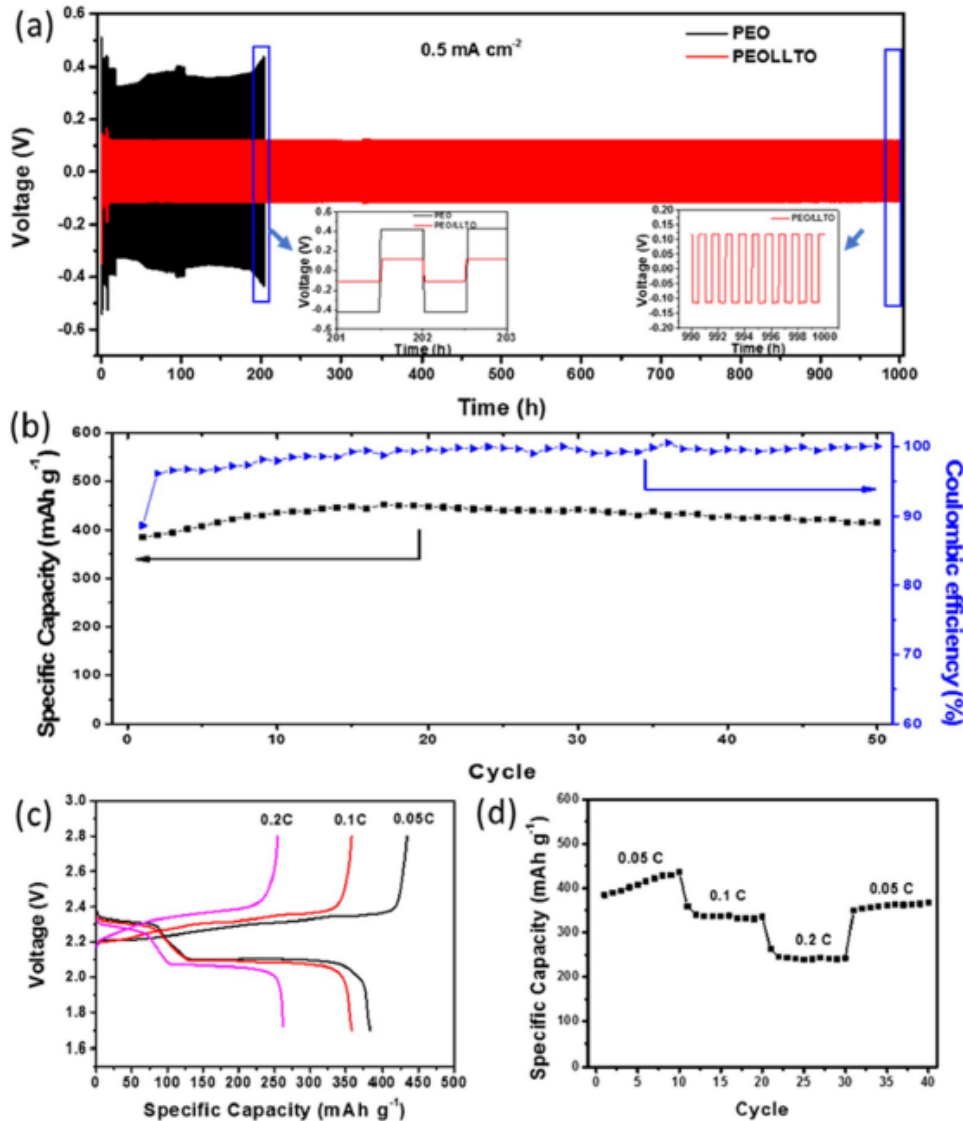
Half Cell & Li-S Full Cells:

Half Cell

- Li/PEO/Li and Li/ (PEO/LLTO)/Li cells tested at a current density of 0.5 mA cm^{-2}
- The Li/PEO/Li :large voltage of around 450 mV in initial cycles.
- Li/(PEO/LLTO)/Li cell: much smaller voltage of around 200 mV in initial cycles.

Li-S Full Cell

- **Stable cycling performance @0.05C**
 - 415 mAh g^{-1} up to 50 cycles
 - Coulombic efficiency remained over 98% after 8 cycles and over 99% after 50 cycles.
- **Remarkable rate capability**
 - 384 mAh g^{-1} @ 0.05C
 - 358 mAh g^{-1} @ 0.1C
 - 262 mAh g^{-1} @ 0.2C



Collaboration and Coordination with Other Institutions



U.S. Department of Energy
-Sponsorship, steering



West Virginia University - Project lead
Management and coordination; inorganic nanofiber design, synthesis and characterization; composite electrolyte development; and battery construction and testing



North Carolina State University - Key partner
Polymer matrix design, synthesis and characterization; linker development; and full cell construction and testing



Quzhou University
Theory calculations on the cationic and anionic doping of perovskite materials

Remaining Challenges and Barriers

- A grafting agent with high ionic conductivity is expected to promote the Li ion transport between the ceramic nanofibers and the polymer matrix. However, such an organic linker is rare.
- It is essential to optimize the interface between the electrolyte and the electrode, decrease interface resistance, which has significant effect on the performance of full-cell batteries.
- It is challenging to improve the life time and capacity of battery performance.

Proposed Future Research

Any proposed future work is subject to change based on funding levels

Composite electrolytes:

- Search for grating agents with high ionic conductivity
- Modify the ceramic nanofiber surface to create a buffer layer at the ceramic-polymer interface
- Optimize the ionic conductivity of the composite electrolyte.

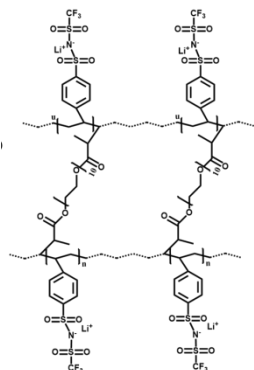
Batteries:

- Optimize the composition and structure of the full cells
- Optimize the interface between electrolyte and electrode

Summary

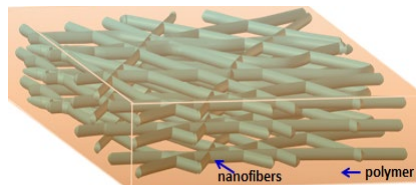
For polymer matrix:

- Two major polymer matrices have been successfully synthesized
- The Plastic crystal-added solid polymer electrolyte exhibits an ionic conductivity of 8.3×10^{-4} S/cm at room temperature



For Composite electrolyte:

- The composite solid electrolyte, which consists of the silane-grafted $\text{Li}_{6.28}\text{La}_3\text{Al}_{0.24}\text{Zr}_2\text{O}_{12}$ (s@LLAZO) nanofibers and the poly(ethylene glycol) diacrylate (PEGDA) has been developed, shows an ionic conductivity of 4.9×10^{-4} S/cm and a stable electrochemical window.
- The composite electrolyte, which consists of Li_3PO_4 -modified LLATO nanofibers and PVDF-HFP, exhibits ionic conductivity of 5.1×10^{-4} S/cm, as well as stable and wide electrochemical window. The Li^+ ion transport pathways have been investigated.



For Full cells:

- **Li|s@LLAZO(6h)-60PEGDA|LFP cell:** Discharge capacities of 158, 147, 135, 113, and 78 mAh g⁻¹ were obtained at rates of 0.2, 0.5, 1, 2, and 5 C, respectively. Even at a high current density of 10 C, the cell delivers a capacity of 44 mAh g⁻¹, showing stable cycling performance for 200 cycles.
- **Li|PVDF-HFP/LiTFSI/LLATO/Li₃PO₄|LFP cell:** Discharge capacities of 158, 147, 133, 98, 76 mAh g⁻¹ were obtained at rates of 0.1, 0.2, 0.5, 1, and 2C, respectively.
- **Flexible CNF/S-PEO/LLTO bilayer Li-S batteries:** Discharge capacities of 384, 358, 262 mAh g⁻¹ were obtained at rates of 0.05, 0.1, 0.2C, respectively, showing stable cycling performance for 50 cycles.

